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Neural Network Based Correlations for Estimating the First and Second Dissociation Constant of Carbonic Acid in Seawater

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Neural Network (NN) can be used successfully in modelling, simulation and optimisation of desalination processes. In this paper, three NN based correlations are developed for predicting the first dissociation constant (K_1) and the second dissociation constant (K_2) of carbonic acid in seawater as function of temperature and salinity. These correlations are developed from different sources of the experimental data from the literature. It is found that the NN based correlation can predict K_1 and K_2 very close to the experimental data. These correlations are currently being implemented in the full MSF (Multi-Stage Flash) desalination process model for performance evaluation of the process which will be reported elsewhere.

1. Introduction

The main technologies used for desalination are thermal processes and reverse osmosis. Both suffer from scale formation and fouling problems. The major problems encountered with scale formation in desalination plants include significant reduction in the thermal performance of the plant (Al-Ahmad, 2008). Main types of scales in thermal desalination plants are $CaCO_3$, $Mg(OH)_2$ and $CaSO_4$ (Al-Ahmad and Aleem, 1993). Although there is some work which has been done on the development and testing anti-scale agents in thermal desalination plants, very little work has been devoted to the understanding of the mechanism of scale formation. The formation of $CaCO_3$ in thermal desalination plants strongly depends on the concentrations of HCO^-_3, temperature, pH, and the rate of CO_2 release rate. The HCO^-_3 concentration in seawater is the key factor in the process of $CaCO_3$ scale formation (El-Din and Mohammed, 1989).

Better knowledge of K_1 and K_2 in seawater water is needed to describe the carbonate system of seawater, CO_2 release process, and of scaling tendency of $CaCO_3$ in MSF and MEE distillers. Calculation of K_1 and K_2 depend on the temperature and salinity of the seawater. Several correlations listed in Table 1 have been developed in the past to calculate K_1 and K_2. Small error in calculating K_1 and K_2 can lead to considerable errors in describing the carbonate system in seawater and calculation of calcium carbonate scaling tendency. Neural networks have been used in all sectors of process engineering such as process modelling, optimisation, design and control (Tanvir and Mujtaba, 2006). In this work, three NN correlations based on three sources of experimental data

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(Millero et al., 1997; Mehrbach et al., 1973; Millero et al., 2006) have developed for estimating K_1 and K_2 in seawater for different salinity and temperature. The ultimate objective is to implement these correlations in the full MSF (Multi-Stage Flash) desalination process model for the performance evaluation of the process.

Table 1. Different correlations for estimating K_1 and K_2 in seawater

Correlation 1: Mehrbach et al. (1973), Data source: Mehrbach et al
$pK_1 = -13.721 + 0.031334 \times T + 3235.76/T + 1.3 \times 10^{-5} \times S \times T - 0.1032 \times S^{0.5}$
$pK_2 = 5371.96 + 1.671221 \times T + 0.22913 \times S + 18.3802 \times \log(S) - 128375.28/T - 2194.30$
$\times \log(T) - 8.0944 \times 10^{-4} \times S \times T - 5617.11 \times \log(S)/T + 2.136 \times S/T$ T in °K, S pp1000
Correlation 2: Millero (1995), Data source: Millero (1995)
$pK_1^{SW} = 2.18867 - 2275.036/T - 1.468\ln(T) + (-0.138681 - 9.33291/T)S^{0.5}$
$+ 0.0726483S - 0.00574938 \times S^{1.5}, K_2^{SW} = -0.84226 - 3741.1288/T - 1.437\ln(T)$
$+ (-0.128417 - 24.41239/T) \times S^{0.5} + 0.1195308S - 0.00912840 \times S^{1.5}$, T in°K , S in g/kg.
Correlation 3 : Mojica et al (2002), Data source: Mojica et al 2002)
$pK_1 = -43.6977 - 0.012903 \times S + 1.364 \times 10^{-4} S^2 + 2885.378/T +$
$7.045159\ln(T)$., $pK_2 = -452.0940 - 13.142162S - 8.101 \times 10^{-4} S^2 +$
$21263.61/T + 68.483143\ln(T) + (-581.4428S + 0.259601S^2)/T -$
$1.967035S\ln(T)$.where, T in°C, S in g/kg.

Note: In all correlations, K_1 and K_2 are on the basis of mol/kg seawater

2. Neural Network Based Correlation for K_1 And K_2

2.1 NN architecture and training

As shown in Figure 1, the neural network architecture can be described by how many layers the network has, the number of neurons in each layer, and how the layers are connected to each other. In this work a multi-layered feed forward network is used and the Levenberg-Marquardt back propagation algorithm is chosen to train the network (Mathlab Toolbox, Hagan et al., 1996).

Neural network based techniques usually requires a large number of data sets. The network calculates the error between the output and the target. This error is fed back to the network and weights and biases are adjusted according to Least Mean Square (LMS) error criteria. The process is continued until the network output is close to the target. This is known as training by back propagation method (as shown in figure 2). Testing the network is a way of checking the performance of a trained network. In the proposed NN based correlations, an optimum number of hidden layers and neurons in each layer is determined by trial and error for each network and the network is fed with the input data (salinity, temperature) to predict the output (K_1 and K_2). A training graph (LMS error vs. time) is used to find how long it takes to get a good NN architecture and how many times the network needs to re-initialize the weights and biases.

All the input data has been scaled, so that they will have zero mean and standard deviation equal to 1, to find the most accurate neural network relationship for input/output relationship. The NN predicted output value is rescaled to its original units.

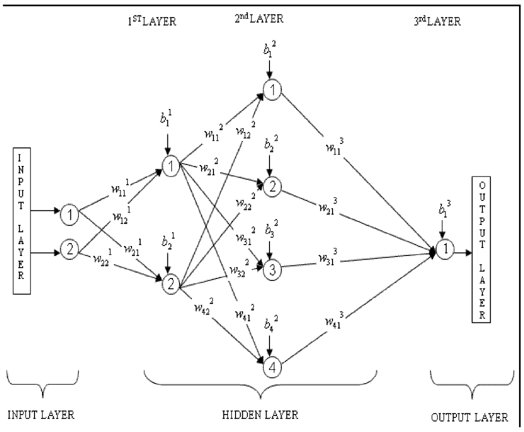

Figure 1 A three layer NN

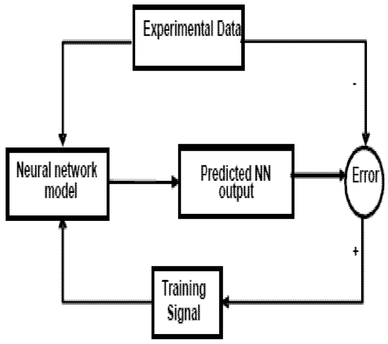

Figure 2 Back-propagation training

2.2 NN based correlations for different data set

In this work, we developed 3 different NN based correlations to estimate the first dissociation constant K_1 and the second dissociation K_2. Theses correlations (NN1_K1 and NN1_K2) are based on the data source from Millero (1997), (NN2_K1 and NN2_K2) are based on the data source from Mehrbach et al. (1973) and (NN3_K1 and NN3_K2) are based on the data source from Millero et al. (2006). In these NN based correlations, the number of neurons in the first layer, hidden layer and third layer were found 2, 4, and 1 respectively (Figure 1). Between the input and first layer, the transfer function was tangent function and between the first and second layer was purline. In addition, the transfer function between the second and third function was purline. For each of the NN based correlations, first 2 input data points are selected for training, the next input data point for validation and the fourth one is selected for testing the correlations. This selection process continues sequentially until all the data points are exhausted. Thus, the total input data are divided into three sets: training (50%), validation (25%), and testing (25%) datasets. Please refer to original references for the data used and also Said (2010).

3. Results And Discussions

Sample experimental data from different sources and predictions by different NN based correlations are shown in Figures 3-8. For each data source, the corresponding NN based correlation predicted the K1 and K2 values close to the experiment data. Each correlation was also used to predict K_1 and K_2 values based on (salinity, temperature) which were never used for training, validation or testing the correlation. For example, NN1_K1 and NN1_K2 is used to Predict K_1 and K_2 at T40ºC= at different salinity values (Figures 3 and 4); NN2_K1 and NN2_K2 is used to predict K_1 and K_2 at T35ºC

= at different salinity values (figures 5 and 6); and NN3_K1 and NN3_K3 is used to predict K_1 and K_2 at T= 50ºC at different salinity values (Figure 7 and 8). The results clearly show that the predictions by the correlations follow the expected trends.

It would be interesting at this point to investigate how different NN based correlations predict K_1 and K_2 values using the (temperature, salinity) data from sources other than the sources used to develop the correlation using the same range. For example NN1_K1 and NN1_K2 correlations were developed using the temperature range 1ºC < T < 40 ºC, and salinity 5<S<35. NN1_K1 and NN1_K2 are now used to predict K_1 and K_2 values using Mehrbach data within the range of 0ºC < T <30ºC, and salinity 19 < S <43. Similarly prediction of K_1 and K_2 by (NN1_K1, NN1_K2) using Millero (2006) data within the range of 0 ºC < T < 50 ºC, and salinity 1< S <50. Note that the predictions of K_1 and K_2 by NN1_K1 and NN1_K2 were found to be close to Millero (2006) data. Also the predictions of K_1 and K_2 by NN2_K1 and NN2_K2 were found to be close to Millero (2006) data (Said, 2010). However, the predictions of K_1 by NN1_K1 were not as close as expected to the experimental data by Mehrbach data. Also predictions of K_1 and K_2 by NN3_K1 and NN3_K2 were not close to experimental K_1 and K_2 by Mehrbach data.

4. Conclusions

Three NN based correlations for predicting the first and second dissociation constants (K_1, K_2) of carbonic acid in seawater have been developed. For each correlation, a multi-layered feed forward network trained with back propagation method is used. It is found that the NN based correlations can predict the experimental K_1 and K_2 very closely to the values of K_1 and K_2 obtained by using correlations from literature. It is found that, the NN1_K1 and NN1_K2 developed based on experimental data of Millero (1997) can predicted the values of K_1 and K_2 when compared with NN2_K1, NN2_K2, NN3_K1 and NN3_K2 correlations. The neural network based correlations developed in this work can predict the values of K_1 and K_2 for temperature less than or equal 50 ºC based on the experimental data available. Multistage flash (MSF) plants usually operate at temperature as high as 90 ºC. Therefore, the extrapolation of the NN correlations will be used to adequate the MSF temperature conditions and its usefulness in evaluating the performance of MSF process will be assessed.

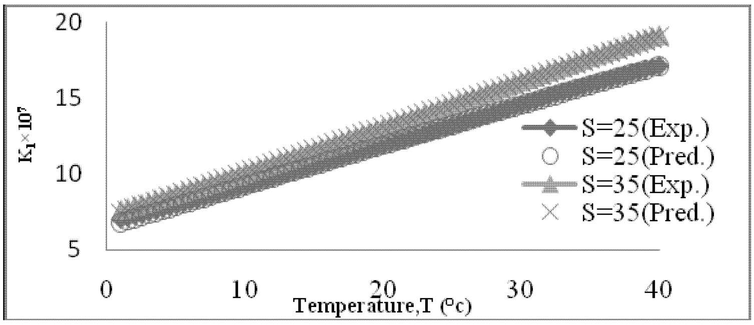

Figure 3 Experimental K_1 by Millero et al. (1997) and Prediction by NN1_K1

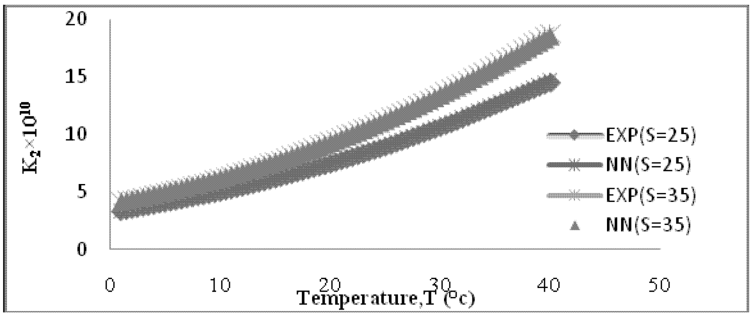

Figure 4 Experimental K_2 by Millero et al. (1997) and Prediction by NN1_K2

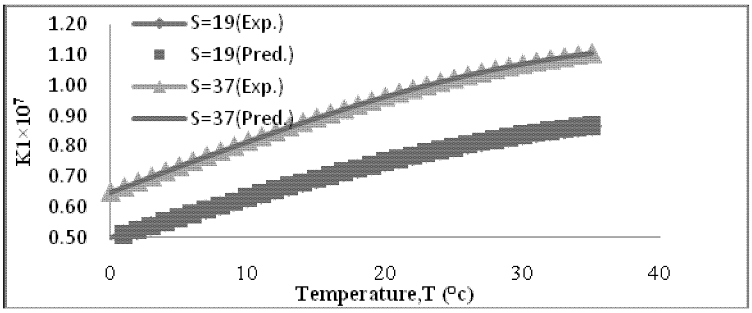

Figure 5 Experimental K_1 by Mehrbach et al. (1973) and Prediction by NN2_K1

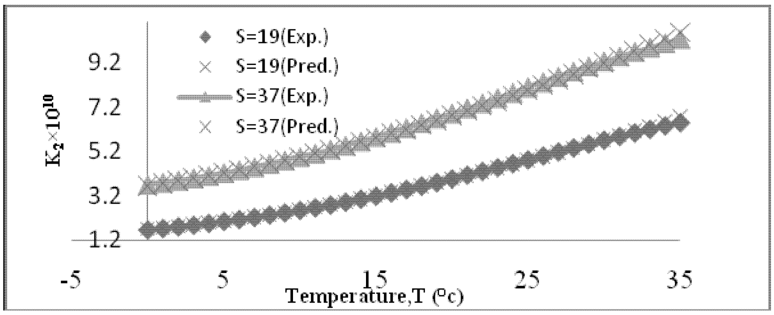

Figure 6 Experimental K_2 by Mehrbach et al. (1973) and Prediction by NN2_K2

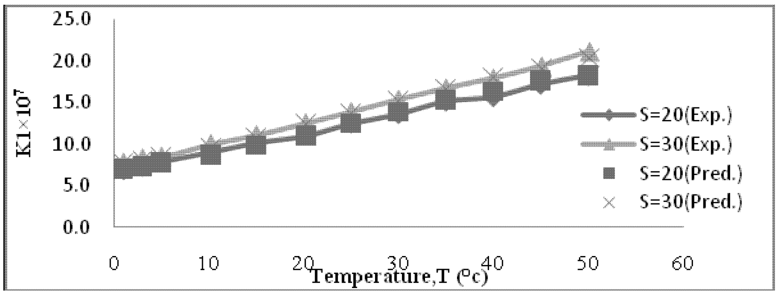

Figure 7 Experimental K_1 by Millero et al. (2006) and Prediction by NN3_K1

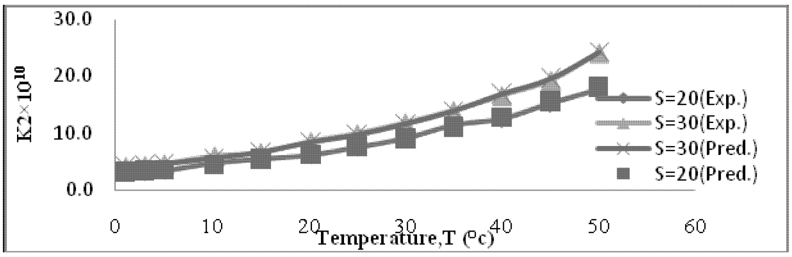

Figure 8 Experimental K_2 by Millero et al. (1997) and Prediction by NN3_K2

References

Al-Ahmad A. and Abdul Aleem F., 1993, Scale formation and fouling problems effect on the performance of MSF and RO desalination plants in Saudi Arabia, Desalination, 93, 287-310.

Al-Ahmad A., 2008, Factors Affecting Scale Formation in Sea Water Environments – An Experimental Approach, Chemical Engineering Technology, 31(1), 149-156.

Mehrbach C., Culberson C.H., and Hawley J.E., 1973, Measurements of the apparent dissociation constant of carbonic acid in seawater at atmospheric pressure, Limnology and Oceanography, 18, 897-907.

Millero F.J. and Roy R.N., 1997, A chemical equilibrium model for the carbonate system in natural water, Croatia Chemica Acta, 70, 1-38.

Millero F. J., Graham T. B., Huang F., Bustos-Serrano H., and Pierrot D., 2006, Dissociation constants of carbonic acid in seawater as a function of salinity and temperature, Marine Chemistry, 100, 80-94.

Mojica F.J. and Millero F.J, 2002, The of pK_1+pk_2 for the dissociation of carbonic acid in seawater, Geochimica et Cosmochimica Acta, 66, 2529-2540.

Hagan M. T., Domuth H.B., and Beal M.H., 1996, Neural Network Design, Boston: PWS.

Said S.A., 2010, Modelling and simulation of the effect of non-condensable gases on the performance of MSF desalination process, Internal Report, University Bradford, UK

Shams El-Din A.M. and Mohammed R.A., 1989, The problem of alkaline scale formation from a study on Arabian Gulf water, Desalination, 71, 313-324.

Tanvir M.S. and Mujtaba I.M., 2006, Neural network based correlations for estimating temperature elevation for seawater in MSF desalination process, Desalination, 195, 251-272.